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## 2 DFT calculation for 2-$OCHCH_2$

**29**

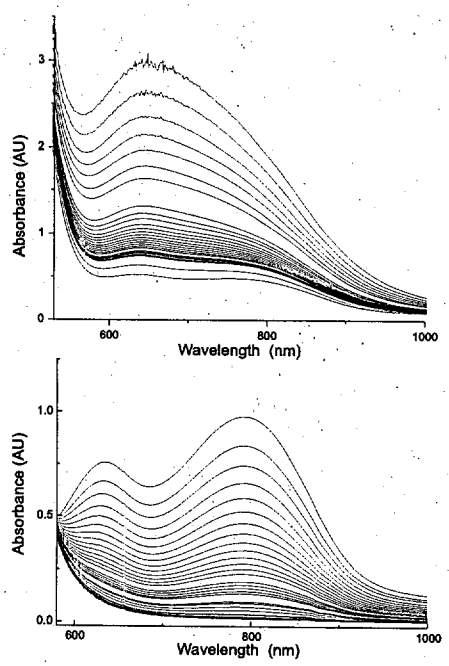



Figure 1: Decay of $Ti(NRAr^1)_3$ (**1**) monitored by UV-vis spectroscopy: reaction with a 1,4-diketone (top); reaction with bromo-benzene – typical decay (bottom).

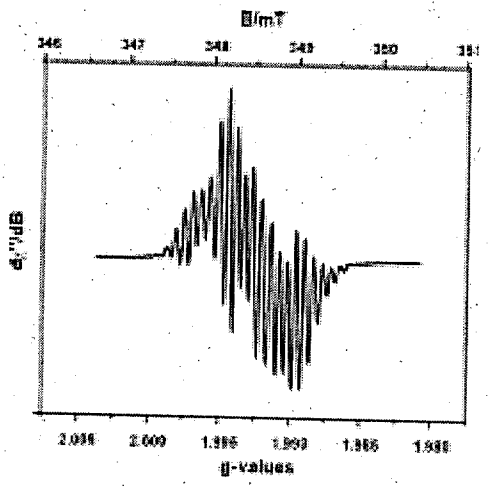
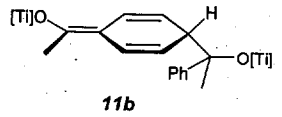



Figure 2: EPR spectrum of **1**-$OCPh_2$, toluene, 25 °C).




***11b***

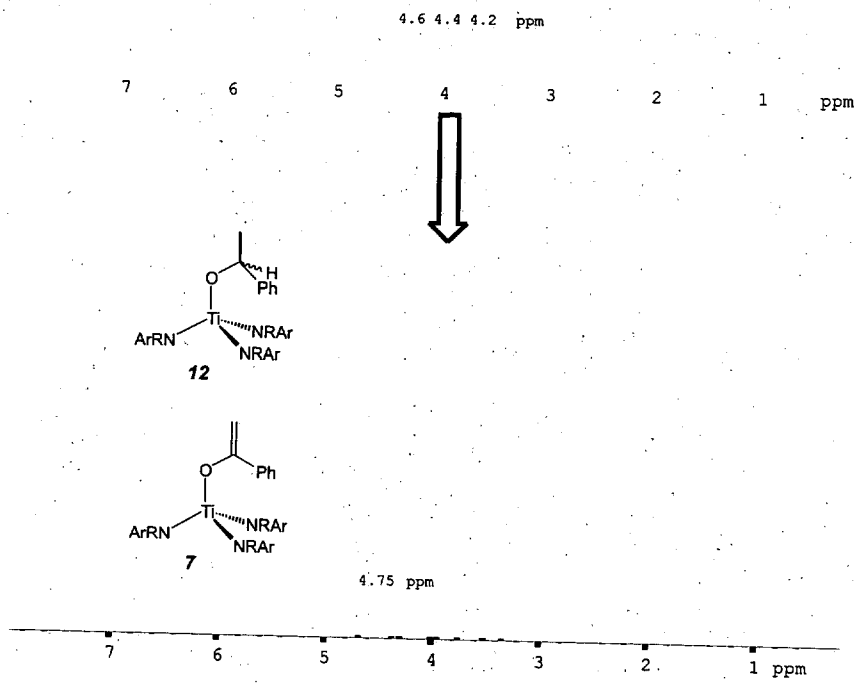



Figure 3: $^1$H NMR spectra ($CDCl_3$) of the Gomberg-like dimer (**1**-OCMePh)$_2$ (top) and its disproportionation products, enolate **1**-OC($CH_2$)Ph and alkoxide **1**-OCHMePh (bottom).

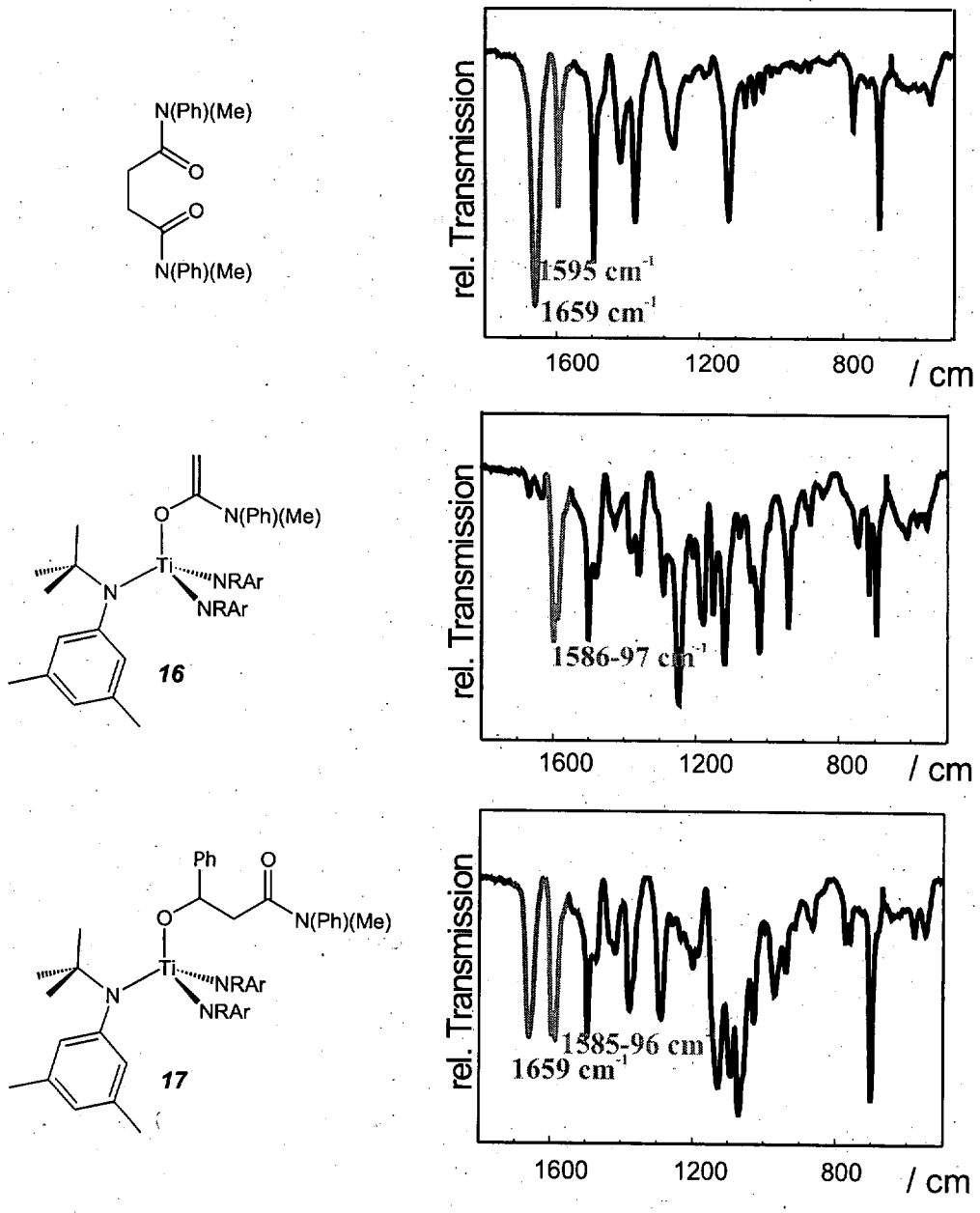



Figure 4: Infrared spectra ($C_6D_6$, KBr plates) of succinic acid di-amide (top), amide enolate **1**-$OC(CH_2)NPhMe$ (center) and aldol condesation product **1**-$OCHPh(CH_2CONPhMe)$ (bottom).

Table 1: Atomic coordinates [ x $10^4$] and equivalent isotropic displacement parameters [$Å^2$ x $10^3$] for 1-$OC(CH_2)NPhMe$. $U$(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Ti | 783(1) | 1605(1) | 2314(1) | 27(1) |
| O | 2014(2) | 207(2) | 2147(2) | 35(1) |
| N(2) | -663(3) | 1469(2) | 3007(2) | 30(1) |
| N(3) | 1499(3) | 2619(2) | 2837(2) | 29(1) |
| C(31) | 1140(3) | 3791(3) | 2592(2) | 31(1) |
| N(1) | 177(3) | 2259(3) | 1258(2) | 30(1) |
| C(310) | 2460(4) | 1208(3) | 3914(3) | 43(1) |
| C(11) | -1171(4) | 2767(4) | 1168(2) | 35(1) |
| C(35) | 1579(4) | 5342(3) | 1841(3) | 41(1) |
| C(46) | 3594(5) | -1928(4) | 4183(3) | 59(1) |
| C(39) | 2298(5) | 3201(4) | 4111(3) | 68(2) |
| C(21) | -1397(4) | 2423(3) | 3525(2) | 33(1) |
| C(34) | 407(4) | 6057(3) | 2153(3) | 42(1) |
| C(44) | 5496(5) | -1476(5) | 4028(3) | 69(2) |
| N(4) | 4052(3) | -1097(3) | 1990(2) | 51(1) |
| C(42) | 4272(4) | -1345(3) | 2839(3) | 41(1) |
| C(48) | 5065(5) | -1021(5) | 1415(3) | 75(2) |
| C(27) | -1078(4) | 440(3) | 3155(2) | 37(1) |
| C(411) | 2415(5) | -1218(4) | 1145(3) | 51(1) |
| C(22) | -1027(4) | 2580(3) | 4315(2) | 38(1) |
| C(19) | 2395(4) | 1776(4) | 643(3) | 44(1) |
| C(17) | 997(4) | 2280(3) | 460(2) | 36(1) |
| C(210) | -656(5) | -92(4) | 3994(3) | 57(1) |
| C(32) | -26(4) | 4534(3) | 2892(2) | 38(1) |

| | | | | |
|---|---|---|---|---|
| C(47) | 3408(4) | -1709(4) | 3341(3) | 47(1) |
| C(37) | 2521(4) | 2268(3) | 3457(2) | 35(1) |
| C(33) | -407(4) | 5673(3) | 2676(3) | 43(1) |
| C(36) | 1931(4) | 4210(3) | 2065(2) | 39(1) |
| C(29) | -2515(4) | 746(4) | 3140(3) | 64(1) |
| C(43) | 5326(4) | -1242(4) | 3189(3) | 52(1) |
| C(41) | 2784(4) | -715(3) | 1739(2) | 37(1) |
| C(351) | 2473(5) | 5771(4) | 1266(3) | 65(2) |
| C(38) | 3850(4) | 2004(4) | 3006(3) | 60(1) |
| C(331) | -1675(4) | 6468(4) | 3031(4) | 72(2) |
| C(24) | -2804(4) | 4275(4) | 4519(3) | 51(1) |
| C(23) | -1715(4) | 3503(4) | 4817(3) | 46(1) |
| C(28) | -463(4) | -421(4) | 2461(3) | 51(1) |
| C(18) | 708(4) | 1560(4) | -213(2) | 47(1) |
| C(26) | -2496(4) | 3210(3) | 3253(3) | 41(1) |
| C(110) | 760(4) | 3484(4) | 135(3) | 48(1) |
| C(25) | -3213(4) | 4134(4) | 3747(3) | 48(1) |
| C(12) | -1766(4) | 3932(4) | 1231(2) | 44(1) |
| C(16) | -1923(4) | 2098(4) | 1019(2) | 43(1) |
| C(15) | -3227(4) | 2558(5) | 957(3) | 55(1) |
| C(13) | -3063(4) | 4426(4) | 1128(3) | 55(1) |
| C(14) | -3774(5) | 3719(5) | 1003(3) | 65(2) |
| C(45) | 4641(5) | -1813(5) | 4528(3) | 67(2) |
| C(231) | -1262(5) | 3640(4) | 5669(3) | 70(2) |
| C(251) | -4426(5) | 4959(4) | 3449(3) | 73(2) |
| C(131) | -3671(5) | 5696(5) | 1157(4) | 84(2) |
| C(151) | -4045(5) | 1821(5) | 855(3) | 79(2) |

Table 2: Bond lengths [Å] and angles [°] for **1**-$OC(CH_2)NPhMe$.

| | |
|---|---|
| Ti-O | 1.847(3) |
| Ti-N(3) | 1.931(3) |
| Ti-N(1) | 1.931(3) |
| Ti-N(2) | 1.936(3) |
| O-C(41) | 1.340(4) |
| N(2)-C(21) | 1.444(5) |
| N(2)-C(27) | 1.510(5) |
| N(3)-C(31) | 1.444(5) |
| N(3)-C(37) | 1.510(5) |
| C(31)-C(32) | 1.385(5) |
| C(31)-C(36) | 1.390(5) |
| N(1)-C(11) | 1.440(5) |
| N(1)-C(17) | 1.519(4) |
| C(310)-C(37) | 1.520(5) |
| C(11)-C(16) | 1.392(5) |
| C(11)-C(12) | 1.394(6) |
| C(35)-C(34) | 1.383(6) |
| C(35)-C(36) | 1.389(5) |
| C(35)-C(351) | 1.520(6) |
| C(46)-C(45) | 1.370(7) |
| C(46)-C(47) | 1.386(6) |
| C(39)-C(37) | 1.530(6) |
| C(21)-C(26) | 1.388(5) |
| C(21)-C(22) | 1.393(5) |
| C(34)-C(33) | 1.380(6) |
| C(44)-C(45) | 1.362(7) |
| C(44)-C(43) | 1.381(6) |
| N(4)-C(42) | 1.408(5) |
| N(4)-C(41) | 1.417(5) |
| N(4)-C(48) | 1.427(5) |
| C(42)-C(43) | 1.377(6) |
| C(42)-C(47) | 1.389(6) |
| C(27)-C(28) | 1.523(5) |
| C(27)-C(29) | 1.517(6) |
| C(27)-C(210) | 1.523(6) |
| C(411)-C(41) | 1.309(5) |

| | |
|---|---|
| C(22)-C(23) | 1.391(5) |
| C(19)-C(17) | 1.520(5) |
| C(17)-C(18) | 1.531(5) |
| C(17)-C(110) | 1.530(6) |
| C(32)-C(33) | 1.393(5) |
| C(37)-C(38) | 1.531(6) |
| C(33)-C(331) | 1.513(6) |
| C(24)-C(25) | 1.379(6) |
| C(24)-C(23) | 1.389(6) |
| C(23)-C(231) | 1.519(6) |
| C(26)-C(25) | 1.393(6) |
| C(25)-C(251) | 1.510(6) |
| C(12)-C(13) | 1.390(6) |
| C(16)-C(15) | 1.384(6) |
| C(15)-C(14) | 1.381(7) |
| C(15)-C(151) | 1.507(7) |
| C(13)-C(14) | 1.387(7) |
| C(13)-C(131) | 1.511(7) |
| O-Ti-N(3) | 109.85(12) |
| O-Ti-N(1) | 110.59(12) |
| N(3)-Ti-N(1) | 107.84(13) |
| O-Ti-N(2) | 110.51(12) |
| N(3)-Ti-N(2) | 109.90(12) |
| N(1)-Ti-N(2) | 108.08(12) |
| C(41)-O-Ti | 159.0(2) |
| C(21)-N(2)-C(27) | 113.2(3) |
| C(21)-N(2)-Ti | 117.9(2) |
| C(27)-N(2)-Ti | 128.6(2) |
| C(31)-N(3)-C(37) | 114.9(3) |
| C(31)-N(3)-Ti | 120.0(2) |
| C(37)-N(3)-Ti | 124.9(2) |
| C(32)-C(31)-C(36) | 118.3(4) |
| C(32)-C(31)-N(3) | 119.4(3) |
| C(36)-C(31)-N(3) | 122.3(3) |
| C(11)-N(1)-C(17) | 113.6(3) |
| C(11)-N(1)-Ti | 120.2(2) |
| C(17)-N(1)-Ti | 126.2(2) |
| C(16)-C(11)-C(12) | 118.0(4) |
| C(16)-C(11)-N(1) | 120.5(4) |
| C(12)-C(11)-N(1) | 121.5(4) |
| C(34)-C(35)-C(36) | 118.3(4) |

| | |
|---|---|
| C(34)-C(35)-C(351) | 121.5(4) |
| C(36)-C(35)-C(351) | 120.2(4) |
| C(45)-C(46)-C(47) | 120.8(5) |
| C(26)-C(21)-C(22) | 117.9(4) |
| C(26)-C(21)-N(2) | 121.0(3) |
| C(22)-C(21)-N(2) | 121.0(3) |
| C(35)-C(34)-C(33) | 121.7(4) |
| C(45)-C(44)-C(43) | 121.7(5) |
| C(42)-N(4)-C(41) | 119.6(3) |
| C(42)-N(4)-C(48) | 120.2(4) |
| C(41)-N(4)-C(48) | 119.1(4) |
| C(43)-C(42)-N(4) | 121.8(4) |
| C(43)-C(42)-C(47) | 118.6(4) |
| N(4)-C(42)-C(47) | 119.6(4) |
| N(2)-C(27)-C(28) | 109.2(3) |
| N(2)-C(27)-C(29) | 111.0(3) |
| C(28)-C(27)-C(29) | 107.9(3) |
| N(2)-C(27)-C(210) | 110.2(3) |
| C(28)-C(27)-C(210) | 108.9(4) |
| C(29)-C(27)-C(210) | 109.6(4) |
| C(23)-C(22)-C(21) | 121.6(4) |
| C(19)-C(17)-N(1) | 108.7(3) |
| C(19)-C(17)-C(18) | 108.8(3) |
| N(1)-C(17)-C(18) | 109.4(3) |
| C(19)-C(17)-C(110) | 108.7(3) |
| N(1)-C(17)-C(110) | 111.7(3) |
| C(18)-C(17)-C(110) | 109.4(3) |
| C(33)-C(32)-C(31) | 121.3(4) |
| C(46)-C(47)-C(42) | 120.2(4) |
| N(3)-C(37)-C(39) | 110.0(3) |
| N(3)-C(37)-C(310) | 109.8(3) |
| C(39)-C(37)-C(310) | 107.8(3) |
| N(3)-C(37)-C(38) | 110.7(3) |
| C(39)-C(37)-C(38) | 110.5(4) |
| C(310)-C(37)-C(38) | 108.1(3) |
| C(34)-C(33)-C(32) | 118.7(4) |
| C(34)-C(33)-C(331) | 121.3(4) |
| C(32)-C(33)-C(331) | 120.0(4) |
| C(35)-C(36)-C(31) | 121.7(4) |
| C(42)-C(43)-C(44) | 120.0(4) |
| C(411)-C(41)-O | 123.4(4) |

| | |
|---|---|
| C(411)-C(41)-N(4) | 122.1(4) |
| O-C(41)-N(4) | 114.5(3) |
| C(25)-C(24)-C(23) | 121.3(4) |
| C(24)-C(23)-C(22) | 118.6(4) |
| C(24)-C(23)-C(231) | 121.9(4) |
| C(22)-C(23)-C(231) | 119.5(4) |
| C(21)-C(26)-C(25) | 121.6(4) |
| C(24)-C(25)-C(26) | 118.9(4) |
| C(24)-C(25)-C(251) | 120.5(4) |
| C(26)-C(25)-C(251) | 120.6(4) |
| C(13)-C(12)-C(11) | 121.6(4) |
| C(11)-C(16)-C(15) | 121.8(4) |
| C(14)-C(15)-C(16) | 118.3(4) |
| C(14)-C(15)-C(151) | 120.3(5) |
| C(16)-C(15)-C(151) | 121.4(5) |
| C(14)-C(13)-C(12) | 118.0(5) |
| C(14)-C(13)-C(131) | 121.5(5) |
| C(12)-C(13)-C(131) | 120.5(5) |
| C(13)-C(14)-C(15) | 122.1(4) |
| C(44)-C(45)-C(46) | 118.7(5) |

Table 3: Anisotropic displacement parameters [$Å^2$ x $10^3$] for **1**-$OC(CH_2)NPhMe$.

| | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| Ti | 27(1) | 28(1) | 27(1) | 0(1) | -2(1) | -10(1) |
| O | 37(2) | 31(2) | 35(2) | -2(1) | -3(1) | -8(1) |
| N(2) | 33(2) | 32(2) | 25(2) | -1(1) | -3(1) | -12(2) |
| N(3) | 27(2) | 27(2) | 31(2) | 1(1) | -5(1) | -9(1) |
| C(31) | 29(2) | 34(2) | 32(2) | 2(2) | -10(2) | -11(2) |
| N(1) | 26(2) | 38(2) | 26(2) | 0(1) | -1(1) | -11(2) |
| C(310) | 50(3) | 38(3) | 38(2) | 1(2) | -8(2) | -8(2) |
| C(11) | 29(2) | 48(3) | 27(2) | 2(2) | -1(2) | -11(2) |
| C(35) | 43(3) | 36(3) | 45(3) | 5(2) | -6(2) | -14(2) |
| C(46) | 55(3) | 54(3) | 59(3) | 18(2) | 5(3) | -7(3) |
| C(39) | 96(4) | 39(3) | 68(3) | -4(2) | -47(3) | -9(3) |
| C(21) | 33(2) | 33(2) | 33(2) | -1(2) | 6(2) | -14(2) |
| C(34) | 45(3) | 26(2) | 53(3) | 2(2) | -11(2) | -8(2) |
| C(44) | 42(3) | 92(4) | 64(4) | -5(3) | -11(3) | -8(3) |
| N(4) | 36(2) | 69(3) | 43(2) | 1(2) | 7(2) | -10(2) |
| C(42) | 31(2) | 40(3) | 45(3) | -3(2) | 2(2) | -3(2) |
| C(48) | 43(3) | 112(5) | 62(3) | 10(3) | 12(3) | -20(3) |
| C(27) | 44(3) | 37(2) | 35(2) | -3(2) | 2(2) | -23(2) |
| C(411) | 61(3) | 49(3) | 45(3) | -16(2) | 5(2) | -21(2) |
| C(22) | 39(2) | 37(2) | 36(2) | -2(2) | 1(2) | -11(2) |
| C(19) | 35(2) | 53(3) | 41(2) | 5(2) | 2(2) | -15(2) |
| C(17) | 30(2) | 49(3) | 27(2) | 3(2) | 1(2) | -13(2) |
| C(210) | 86(4) | 45(3) | 48(3) | 4(2) | -2(3) | -34(3) |
| C(32) | 31(2) | 38(3) | 45(2) | 2(2) | -2(2) | -11(2) |
| C(47) | 39(3) | 49(3) | 51(3) | 8(2) | -1(2) | -11(2) |
| C(37) | 39(2) | 30(2) | 36(2) | -1(2) | -10(2) | -10(2) |
| C(33) | 36(2) | 32(2) | 56(3) | -1(2) | -2(2) | -4(2) |
| C(36) | 35(2) | 36(2) | 43(2) | 1(2) | -1(2) | -9(2) |
| C(29) | 48(3) | 67(3) | 88(4) | -9(3) | 4(3) | -33(3) |
| C(43) | 35(3) | 63(3) | 54(3) | -4(2) | 2(2) | -10(2) |
| C(41) | 35(2) | 37(2) | 39(2) | -2(2) | 3(2) | -13(2) |
| C(351) | 58(3) | 47(3) | 87(4) | 22(3) | 12(3) | -18(3) |
| C(38) | 35(3) | 75(4) | 73(3) | 25(3) | -20(2) | -19(2) |
| C(331) | 51(3) | 42(3) | 109(5) | 4(3) | 11(3) | 2(2) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(24) | 54(3) | 40(3) | 50(3) | -11(2) | 19(2) | -8(2) |
| C(23) | 58(3) | 40(3) | 39(2) | -10(2) | 7(2) | -18(2) |
| C(28) | 66(3) | 43(3) | 52(3) | -10(2) | 7(2) | -30(2) |
| C(18) | 49(3) | 62(3) | 31(2) | -6(2) | 3(2) | -20(2) |
| C(26) | 37(3) | 45(3) | 37(2) | 2(2) | 4(2) | -11(2) |
| C(110) | 45(3) | 56(3) | 43(3) | 15(2) | -2(2) | -18(2) |
| C(25) | 35(3) | 44(3) | 56(3) | 3(2) | 14(2) | -4(2) |
| C(12) | 41(3) | 55(3) | 34(2) | 3(2) | 0(2) | -15(2) |
| C(16) | 36(3) | 65(3) | 30(2) | 2(2) | 0(2) | -22(2) |
| C(15) | 37(3) | 96(4) | 35(3) | -3(3) | 0(2) | -27(3) |
| C(13) | 36(3) | 69(4) | 47(3) | 14(2) | 5(2) | 0(3) |
| C(14) | 29(3) | 110(5) | 46(3) | 13(3) | -1(2) | -11(3) |
| C(45) | 50(3) | 89(4) | 49(3) | 12(3) | -8(3) | -4(3) |
| C(231) | 92(4) | 57(3) | 52(3) | -23(3) | -1(3) | -13(3) |
| C(251) | 48(3) | 72(4) | 76(4) | 3(3) | 12(3) | 7(3) |
| C(131) | 55(3) | 84(4) | 85(4) | 23(3) | 9(3) | 13(3) |
| C(151) | 54(3) | 144(6) | 58(3) | -10(3) | 0(3) | -57(4) |

Table 4: Atomic coordinates [ x $10^4$] and equivalent isotropic displacement parameters [$Å^2$ x $10^3$] for 1-$OC(CH_2)Ar^2$. *U*(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| O | 5339(1) | 3173(2) | 1668(1) | 35(1) |
| Ti(1) | 6492(1) | 2846(1) | 1670(1) | 27(1) |
| N(1) | 6540(2) | 2012(2) | 897(1) | 31(1) |
| C(1) | 4695(3) | 3274(3) | 2614(2) | 46(1) |
| N(2) | 7129(2) | 4065(2) | 1640(1) | 31(1) |
| C(2) | 4624(2) | 3181(3) | 1962(2) | 34(1) |
| N(3) | 6999(2) | 2151(2) | 2471(1) | 29(1) |
| C(3) | 3764(2) | 3091(3) | 1495(2) | 36(1) |
| C(4) | 3614(2) | 3531(3) | 876(2) | 46(1) |
| C(5) | 2800(3) | 3429(4) | 453(2) | 60(1) |
| C(6) | 2134(3) | 2880(4) | 625(3) | 62(1) |
| C(7) | 2284(3) | 2456(4) | 1246(3) | 68(1) |
| C(8) | 3089(3) | 2553(3) | 1677(2) | 57(1) |
| C(9) | 1272(3) | 2735(5) | 140(3) | 101(2) |
| C(11) | 7185(2) | 1243(3) | 969(2) | 33(1) |
| C(12) | 6964(2) | 239(3) | 944(2) | 39(1) |
| C(13) | 7601(3) | -490(3) | 1051(2) | 43(1) |
| C(14) | 8476(3) | -215(3) | 1172(2) | 46(1) |
| C(15) | 8723(2) | 769(3) | 1192(2) | 42(1) |
| C(16) | 8068(2) | 1486(3) | 1088(2) | 36(1) |
| C(17) | 5839(2) | 2003(3) | 271(2) | 40(1) |
| C(18) | 5592(3) | 3076(3) | 88(2) | 49(1) |
| C(19) | 5016(2) | 1449(3) | 370(2) | 53(1) |
| C(21) | 7926(2) | 4046(2) | 1377(2) | 33(1) |
| C(22) | 7917(2) | 4104(3) | 698(2) | 37(1) |
| C(23) | 8685(3) | 4106(3) | 447(2) | 45(1) |
| C(24) | 9477(3) | 4071(3) | 891(2) | 50(1) |
| C(25) | 9518(2) | 4014(3) | 1572(2) | 47(1) |
| C(26) | 8739(2) | 3991(3) | 1811(2) | 40(1) |

| | | | | |
|---|---|---|---|---|
| C(27) | 6834(3) | 5100(3) | 1777(2) | 46(1) |
| C(28) | 6349(3) | 5085(3) | 2345(3) | 68(1) |
| C(29) | 7583(4) | 5808(4) | 1928(4) | 108(3) |
| C(31) | 7786(2) | 2492(2) | 2903(2) | 32(1) |
| C(32) | 7287(2) | 358(3) | 2751(2) | 42(1) |
| C(33) | 8490(3) | 3569(3) | 3797(2) | 48(1) |
| C(34) | 9291(3) | 3138(3) | 3758(2) | 50(1) |
| C(35) | 9359(2) | 2394(3) | 3305(2) | 45(1) |
| C(36) | 8603(2) | 2090(3) | 2872(2) | 39(1) |
| C(37) | 6629(2) | 1210(2) | 2709(2) | 32(1) |
| C(38) | 5793(2) | 935(3) | 2213(2) | 39(1) |
| C(39) | 6396(3) | 1368(3) | 3392(2) | 46(1) |
| C(110) | 6191(3) | 1551(4) | -313(2) | 62(1) |
| C(131) | 7326(3) | -1560(3) | 1053(3) | 71(1) |
| C(151) | 9679(3) | 1061(4) | 1307(3) | 68(1) |
| C(210) | 6177(5) | 5460(4) | 1155(3) | 114(3) |
| C(231) | 8650(3) | 4138(4) | -298(2) | 68(1) |
| C(251) | 10397(3) | 3985(4) | 2051(3) | 75(2) |
| C(310) | 7740(2) | 3225(3) | 3374(2) | 40(1) |
| C(331) | 8425(3) | 4377(4) | 4299(2) | 70(1) |
| C(351) | 10230(3) | 1901(4) | 3283(3) | 68(1) |

Table 5: Bond lengths [ Å] and angles [°] for **1**-$OC(CH_2)Ar^2$.

| | |
|---|---|
| O-C(2) | 1.352(4) |
| O-Ti(1) | 1.826(2) |
| Ti(1)-N(3) | 1.904(3) |
| Ti(1)-N(2) | 1.920(3) |
| Ti(1)-N(1) | 1.943(3) |
| N(1)-C(11) | 1.422(4) |
| N(1)-C(17) | 1.491(4) |
| C(1)-C(2) | 1.311(5) |
| N(2)-C(21) | 1.432(4) |
| N(2)-C(27) | 1.511(4) |
| C(2)-C(3) | 1.470(5) |
| N(3)-C(31) | 1.422(4) |
| N(3)-C(37) | 1.508(4) |
| C(3)-C(4) | 1.366(5) |
| C(3)-C(8) | 1.375(5) |
| C(4)-C(5) | 1.375(6) |
| C(5)-C(6) | 1.364(6) |
| C(6)-C(7) | 1.361(7) |
| C(6)-C(9) | 1.497(6) |
| C(7)-C(8) | 1.372(6) |
| C(11)-C(16) | 1.371(5) |
| C(11)-C(12) | 1.394(5) |
| C(12)-C(13) | 1.373(5) |
| C(13)-C(14) | 1.370(5) |
| C(13)-C(131) | 1.504(6) |
| C(14)-C(15) | 1.379(6) |
| C(15)-C(16) | 1.382(5) |
| C(15)-C(151) | 1.493(5) |
| C(17)-C(19) | 1.517(5) |
| C(17)-C(110) | 1.524(5) |
| C(17)-C(18) | 1.524(5) |
| C(21)-C(22) | 1.376(5) |
| C(21)-C(26) | 1.380(5) |
| C(22)-C(23) | 1.376(5) |
| C(23)-C(24) | 1.363(6) |
| C(23)-C(231) | 1.502(6) |
| C(24)-C(25) | 1.372(6) |

| | |
|---|---|
| C(25)-C(26) | 1.379(5) |
| C(25)-C(251) | 1.499(6) |
| C(27)-C(29) | 1.481(6) |
| | |
| C(27)-C(28) | 1.493(5) |
| C(27)-C(210) | 1.529(7) |
| C(31)-C(36) | 1.381(5) |
| C(31)-C(310) | 1.386(5) |
| C(32)-C(37) | 1.521(5) |
| C(33)-C(310) | 1.373(5) |
| C(33)-C(34) | 1.378(6) |
| C(33)-C(331) | 1.509(6) |
| C(34)-C(35) | 1.378(6) |
| C(35)-C(36) | 1.373(5) |
| C(35)-C(351) | 1.504(6) |
| C(37)-C(38) | 1.512(5) |
| C(37)-C(39) | 1.514(5) |
| C(2)-O-Ti(1) | 151.2(2) |
| O-Ti(1)-N(3) | 110.60(11) |
| O-Ti(1)-N(2) | 107.12(11) |
| N(3)-Ti(1)-N(2) | 108.88(12) |
| O-Ti(1)-N(1) | 109.36(11) |
| N(3)-Ti(1)-N(1) | 109.23(12) |
| N(2)-Ti(1)-N(1) | 111.64(12) |
| C(11)-N(1)-C(17) | 116.9(3) |
| C(11)-N(1)-Ti(1) | 118.5(2) |
| C(17)-N(1)-Ti(1) | 123.7(2) |
| C(21)-N(2)-C(27) | 113.3(3) |
| C(21)-N(2)-Ti(1) | 118.5(2) |
| C(27)-N(2)-Ti(1) | 127.7(2) |
| C(1)-C(2)-O | 122.3(3) |
| C(1)-C(2)-C(3) | 122.8(3) |
| O-C(2)-C(3) | 114.9(3) |
| C(31)-N(3)-C(37) | 113.9(3) |
| C(31)-N(3)-Ti(1) | 121.3(2) |
| C(37)-N(3)-Ti(1) | 124.8(2) |
| C(4)-C(3)-C(8) | 118.5(4) |
| C(4)-C(3)-C(2) | 121.5(3) |
| C(8)-C(3)-C(2) | 120.0(3) |
| C(3)-C(4)-C(5) | 119.7(4) |
| C(6)-C(5)-C(4) | 122.1(4) |
| C(7)-C(6)-C(5) | 117.9(4) |

| | |
|---|---|
| C(7)-C(6)-C(9) | 121.1(5) |
| C(5)-C(6)-C(9) | 121.0(5) |
| C(6)-C(7)-C(8) | 121.0(4) |
| C(7)-C(8)-C(3) | 120.8(4) |
| C(16)-C(11)-C(12) | 117.6(3) |
| C(16)-C(11)-N(1) | 119.3(3) |
| C(12)-C(11)-N(1) | 123.0(3) |
| C(13)-C(12)-C(11) | 121.9(3) |
| C(14)-C(13)-C(12) | 118.6(4) |
| C(14)-C(13)-C(131) | 121.7(4) |
| C(12)-C(13)-C(131) | 119.7(4) |
| C(13)-C(14)-C(15) | 121.4(4) |
| C(14)-C(15)-C(16) | 118.7(3) |
| C(14)-C(15)-C(151) | 121.0(4) |
| C(16)-C(15)-C(151) | 120.3(4) |
| C(11)-C(16)-C(15) | 121.7(3) |
| N(1)-C(17)-C(19) | 111.8(3) |
| N(1)-C(17)-C(110) | 110.9(3) |
| C(19)-C(17)-C(110) | 109.9(3) |
| N(1)-C(17)-C(18) | 107.6(3) |
| C(19)-C(17)-C(18) | 109.0(3) |
| C(110)-C(17)-C(18) | 107.5(3) |
| C(22)-C(21)-C(26) | 118.0(3) |
| C(22)-C(21)-N(2) | 122.2(3) |
| C(26)-C(21)-N(2) | 119.8(3) |
| C(23)-C(22)-C(21) | 122.1(4) |
| C(24)-C(23)-C(22) | 118.3(4) |
| C(24)-C(23)-C(231) | 120.9(4) |
| C(22)-C(23)-C(231) | 120.7(4) |
| C(23)-C(24)-C(25) | 121.5(4) |
| C(24)-C(25)-C(26) | 119.1(4) |
| C(24)-C(25)-C(251) | 120.5(4) |
| C(26)-C(25)-C(251) | 120.3(4) |
| C(25)-C(26)-C(21) | 120.9(4) |
| C(29)-C(27)-C(28) | 109.7(4) |
| C(29)-C(27)-N(2) | 112.6(3) |
| C(28)-C(27)-N(2) | 110.1(3) |
| C(29)-C(27)-C(210) | 109.0(5) |
| C(28)-C(27)-C(210) | 107.0(4) |

| | |
|---|---|
| N(2)-C(27)-C(210) | 108.4(4) |
| C(36)-C(31)-C(310) | 118.9(3) |
| C(36)-C(31)-N(3) | 121.0(3) |
| C(310)-C(31)-N(3) | 120.1(3) |
| C(310)-C(33)-C(34) | 118.1(4) |
| C(310)-C(33)-C(331) | 120.3(4) |
| C(34)-C(33)-C(331) | 121.6(4) |
| C(35)-C(34)-C(33) | 122.2(4) |
| C(36)-C(35)-C(34) | 118.5(4) |
| C(36)-C(35)-C(351) | 119.6(4) |
| C(34)-C(35)-C(351) | 121.9(4) |
| C(35)-C(36)-C(31) | 121.1(4) |
| N(3)-C(37)-C(38) | 108.6(3) |
| N(3)-C(37)-C(39) | 110.3(3) |
| C(38)-C(37)-C(39) | 108.5(3) |
| N(3)-C(37)-C(32) | 111.4(3) |
| C(38)-C(37)-C(32) | 108.6(3) |
| C(39)-C(37)-C(32) | 109.3(3) |
| C(33)-C(310)-C(31) | 121.3(4) |

Table 6: Anisotropic displacement parameters [$Å^2$ x $10^3$] for **1**-$OC(CH_2)Ar^2$.

| | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| O | 31(1) | 36(1) | 38(1) | -1(1) | 7(1) | 0(1) |
| Ti(1) | 27(1) | 27(1) | 27(1) | 0(1) | 5(1) | 0(1) |
| N(1) | 30(2) | 31(2) | 30(2) | -2(1) | 3(1) | 3(1) |
| C(1) | 43(2) | 51(2) | 46(2) | 3(2) | 12(2) | 7(2) |
| N(2) | 32(2) | 29(2) | 34(2) | 0(1) | 9(1) | 0(1) |
| C(2) | 31(2) | 30(2) | 44(2) | 2(2) | 12(2) | 4(2) |
| N(3) | 29(2) | 30(2) | 29(2) | 1(1) | 5(1) | -3(1) |
| C(3) | 32(2) | 30(2) | 46(2) | 2(2) | 10(2) | 8(2) |
| C(4) | 39(2) | 51(2) | 48(2) | 2(2) | 10(2) | 5(2) |
| C(5) | 51(3) | 84(3) | 43(2) | 1(2) | 3(2) | 16(2) |
| C(6) | 33(2) | 82(3) | 69(3) | -21(3) | 6(2) | 4(2) |
| C(7) | 40(2) | 75(3) | 88(4) | 1(3) | 12(2) | -10(2) |
| C(8) | 42(2) | 61(3) | 67(3) | 15(2) | 12(2) | -1(2) |
| C(9) | 39(3) | 166(6) | 90(4) | -44(4) | -6(3) | 2(3) |
| C(11) | 36(2) | 35(2) | 26(2) | -3(2) | 5(2) | 4(2) |
| C(12) | 39(2) | 36(2) | 42(2) | -6(2) | 6(2) | -2(2) |
| C(13) | 49(2) | 36(2) | 45(2) | -2(2) | 8(2) | 7(2) |
| C(14) | 48(2) | 45(2) | 45(2) | -4(2) | 8(2) | 16(2) |
| C(15) | 35(2) | 47(2) | 44(2) | -7(2) | 6(2) | 5(2) |
| C(16) | 39(2) | 33(2) | 37(2) | -3(2) | 7(2) | 3(2) |
| C(17) | 41(2) | 47(2) | 29(2) | -4(2) | -2(2) | 7(2) |
| C(18) | 48(2) | 57(3) | 37(2) | 8(2) | -2(2) | 10(2) |
| C(19) | 41(2) | 59(3) | 51(3) | -5(2) | -9(2) | 1(2) |
| C(21) | 36(2) | 25(2) | 39(2) | 0(2) | 13(2) | -5(2) |
| C(22) | 36(2) | 35(2) | 41(2) | -2(2) | 9(2) | -5(2) |
| C(23) | 54(2) | 41(2) | 45(2) | -6(2) | 21(2) | -7(2) |
| C(24) | 42(2) | 50(3) | 66(3) | -8(2) | 28(2) | -9(2) |
| C(25) | 38(2) | 41(2) | 61(3) | -6(2) | 7(2) | -9(2) |
| C(26) | 41(2) | 35(2) | 42(2) | 3(2) | 5(2) | -7(2) |
| C(27) | 55(2) | 29(2) | 59(3) | 0(2) | 23(2) | 3(2) |
| C(28) | 85(3) | 39(2) | 96(4) | -11(2) | 55(3) | -5(2) |
| C(29) | 91(4) | 44(3) | 214(8) | -53(4) | 89(5) | -25(3) |
| C(31) | 35(2) | 32(2) | 27(2) | 7(2) | 2(2) | -7(2) |
| C(32) | 43(2) | 32(2) | 48(2) | 6(2) | 5(2) | -1(2) |
| C(33) | 59(3) | 49(2) | 34(2) | 2(2) | 7(2) | -21(2) |
| C(34) | 46(2) | 57(3) | 40(2) | 6(2) | -6(2) | -21(2) |
| C(35) | 36(2) | 51(2) | 44(2) | 13(2) | -3(2) | -7(2) |
| C(36) | 34(2) | 41(2) | 41(2) | 5(2) | 5(2) | -3(2) |
| C(37) | 35(2) | 27(2) | 36(2) | 7(2) | 9(2) | -4(2) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(38) | 33(2) | 31(2) | 51(2) | 2(2) | 8(2) | -5(2) |
| C(39) | 55(2) | 45(2) | 43(2) | 10(2) | 18(2) | -6(2) |
| C(110) | 73(3) | 76(3) | 32(2) | -5(2) | 3(2) | 21(3) |
| C(131) | 66(3) | 37(3) | 112(4) | -3(3) | 20(3) | 6(2) |
| C(151) | 39(2) | 67(3) | 96(4) | -8(3) | 9(2) | 8(2) |
| C(210) | 174(7) | 76(4) | 86(4) | 15(3) | 12(4) | 75(4) |
| C(231) | 79(3) | 82(3) | 52(3) | -9(2) | 35(2) | -17(3) |
| C(251) | 40(2) | 91(4) | 88(4) | 4(3) | 0(2) | -9(2) |
| C(310) | 43(2) | 41(2) | 34(2) | 3(2) | 8(2) | -7(2) |
| C(331) | 80(3) | 78(3) | 53(3) | -27(3) | 15(2) | -34(3) |
| C(351) | 36(2) | 76(3) | 84(4) | 5(3) | -5(2) | -3(2) |

Table 7: Structural parameters for **1**-$OC(CH_2)Ar^2$ and **1**-$OC(CH_2)NPhMe$ (crystallographically determined) and **2**-$OCHCH_2$ and **2**-$OC(NH_2)CH_2$ (calculated).

| | **1**-$OC(CH_2)Ar^2$ | **2**-$OCHCH_2$ | **1**-$OC(CH_2)NPhMe$ | **2**-$OC(NH_2)CH_2$ |
|---|---|---|---|---|
| Ti-O | 1.826(2) | 1.819 | 1.847(3) | 1.828 |
| C-O | 1.352(4) | 1.353 | 1.340(4) | 1.360 |
| Ti-N (avg.) | 1.922 | 1.920 | 1.933 | 1.917 |
| C=C (enol) | 1.311(5) | 1.337 | 1.309(5) | 1.347 |
| N-C (enol) | | | 1.417(5) | 1.396 |
| O-Ti-N (avg.) | 109 | 109 | 110 | 110 |
| Ti-O-C | 151.2(2) | 151 | 159.0(2) | 141 |
| C(411)-C(41)-N(4)-C(48) | | | 56 | -22 |
| C(411)-C(41)-N(4)-C(42) | | | -112 | -50 |

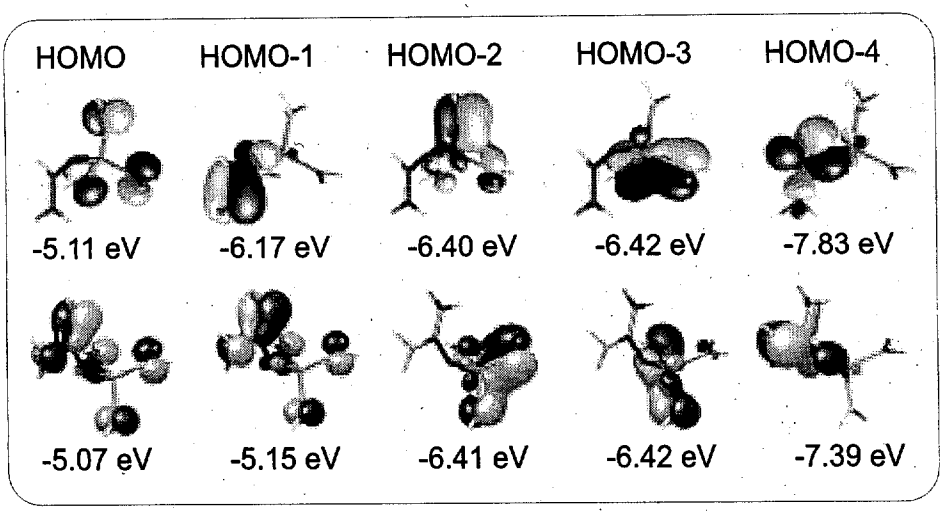



Figure 5: Frontier molecular orbitals of **2**-$OCHCH_2$ (top) and **2**-$OC(NH_2)CH_2$ (bottom).

# 1 DFT calculation for 2-$OC(NH_2)CH_2$

```
 Parallel Execution: Process Information
 =======================================

 Actual Number of Tasks running:     1
 The Master (kid 0) runs on host localhost
(INPUT FILE)
title normal titanium enolate

atoms Z-matrix
1. c 0 0 0 0 0 0
2. c 1 0 0 rCC 0 0
3. o 2 1 0 rCO dd 0
4. ti 3 2 1 rTiO aa 0
5. n 4 3 2 rTiN bb 180
6. n 4 3 2 rTiN bb 300
7. n 4 3 2 rTiN bb 60
8. h 1 2 3 rCH 120 180
9. h 1 2 3 rCH 120 0
10. n 2 1 9 rCN ee 180
11. h 5 4 3 rNH cc 0
12. h 5 4 3 rNH cc 180
13. h 6 4 3 rNH cc 0
14. h 6 4 3 rNH cc 180
15. h 7 4 3 rNH cc 0
16. h 7 4 3 rNH cc 180
17 h 10 2 1 a ff fff
18 h 10 2 1 a gg ggg
end

geovar
rCC 1.31
rCO 1.34
rTiO 1.847
rNH 1.02
rTiN 1.93
rCH 1.01
rCN 1.41
aa 159
bb 109
cc 120
dd 122
```

```
ee 120
a 1
ff 120
gg 120
fff 56
ggg -112
end

Symmetry=NOSYM

fragments
Ti t21.Ti
O t21.O
C t21.C
H t21.H
N t21.N
end

xc
LDA VWN
GRADIENTS BECKE PERDEW
end


relativistic zora

charge 0

corepotentials TAPE12 &
Ti 1
O 2
C 3
H 4
N 5
end

scf
ITERATIONS 99
MIXING 0.05
end

geometry
optim internal selected
end
```

```
end input

 ********************************************************************************
 *                                                                              *
 *  ------------------------------------                                        *
 *   Amsterdam Density Functional  (ADF)          2000.01   17 May, 2000       *
 *  ------------------------------------                                        *
 *                                                                              *
 *                                                                              *
 *                                                                              *
 *                              ================                                *
 *                              |              |                                *
 *                              |     A D F    |                                *
 *                              |              |                                *
 *                              ================                                *
 *                                                                              *
 *                                                                              *
 *                                                                              *
 *   Online information and documentation:  http://www.scm.com                  *
 *   E-mail:  support@scm.com   info@scm.com                                    *
 *                                                                              *
 *                                                                              *
 *   Scientific publications using ADF results must be properly referenced      *
 *   See the User Manuals (or the web site) for recommended citations           *
 *                                                                              *
 ******************************  pentium_linux  *******************************

DF 2000.01  RunTime: Dec08-2000 20:26:57
 normal titanium enolate


 ============================
 A T T A C H E D   F I L E S
 ============================

 Core Potentials:
        file : TAPE12


 ================================
 M O D E L   P A R A M E T E R S
 ================================

 DENSITY FUNCTIONAL POTENTIAL (scf)
```

```
   LDA:                                VWN
   Gradient Corrections:               Becke88 Perdew86

SPIN  (restricted / unrestr.)
   Molecule:                           Restricted
   Fragments:                          Restricted

OTHER ASPECTS
   Relativistic Corrections:           scalar (ZORA,FrozenCore)
   Core Treatment:                     Frozen Orbital(s)

   Electric Field:                     ---

   Magnetic Field:                     ---


Fragment File(s)
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c:
        file : t21.C
        jobid: ADF 2000.01  RunTime: Dec08-2000 20:26:37
        title: Carbon (III, 1s frozen)
o:
        file : t21.O
        jobid: ADF 2000.01  RunTime: Dec08-2000 20:26:30
        title: Oxygen (III, 1s frozen)
ti:
        file : t21.Ti
        jobid: ADF 2000.01  RunTime: Dec08-2000 20:26:26
        title: Titanium (IV, 2p frozen)
n:
        file : t21.N
        jobid: ADF 2000.01  RunTime: Dec08-2000 20:26:48
        title: Nitrogen (III, 1s frozen)h:
h:
       file : t21.H
        jobid: ADF 2000.01  RunTime: Dec08-2000 20:26:41
        title: Hydrogen (III)
```

## 2 DFT calculation for 2-$OCHCH_2$

```
 Parallel Execution: Process Information
 =======================================

 Actual Number of Tasks running:      1
 The Master (kid 0) runs on host localhost
(INPUT FILE)
title normal titanium enolate

atoms Z-matrix
1. c 0 0 0 0 0 0
2. c 1 0 0 rCC 0 0
3. o 2 1 0 rCO dd 0
4. ti 3 2 1 rTiO aa 0
5. n 4 3 2 rTiN bb 180
6. n 4 3 2 rTiN bb 300
7. n 4 3 2 rTiN bb 60
8. h 1 2 3 rCH 120 180
9. h 1 2 3 rCH 120 0
10. h 2 1 9 rCH ee 180
11. h 5 4 3 rNH cc 0
12. h 5 4 3 rNH cc 180
13. h 6 4 3 rNH cc 0
14. h 6 4 3 rNH cc 180
15. h 7 4 3 rNH cc 0
16. h 7 4 3 rNH cc 180
end

geovar
rCC 1.31
rCO 1.35
rTiO 1.82
rNH 1.2
rTiN 1.92
rCH 1
aa 151.2
bb 109
cc 120
dd 122
ee 120
end

Symmetry=C(s)
```

```
fragments
Ti t21.Ti
O t21.O
C t21.C
H t21.H
N t21.N
end

xc
LDA VWN
GRADIENTS BECKE PERDEW
end


relativistic zora

charge 0

corepotentials TAPE12 &
Ti 1
O 2
C 3
H 4
N 5
end

scf
ITERATIONS 99
MIXING 0.05
end

geometry
optim internal selected
end


end input
```

```
*****************************************************************************
*                                                                           *
*  ------------------------------------                                     *
*   Amsterdam Density Functional  (ADF)         2000.01   17 May, 2000      *
*  ------------------------------------                                     *
*                                                                           *
*                                                                           *
*                                                                           *
*                             =================                             *
*                             |               |                             *
*                             |     A D F     |                             *
*                             |               |                             *
*                             =================                             *
*                                                                           *
*                                                                           *
*                                                                           *
*   Online information and documentation:  http://www.scm.com               *
*   E-mail:  support@scm.com   info@scm.com                                 *
*                                                                           *
*                                                                           *
*   Scientific publications using ADF results must be properly referenced   *
*   See the User Manuals (or the web site) for recommended citations        *
*                                                                           *
****************************** pentium_linux *******************************

ADF 2000.01  RunTime: Dec08-2000 00:59:38
normal titanium enolate



============================
A T T A C H E D   F I L E S
============================

Core Potentials:
       file : TAPE12



==============================
M O D E L   P A R A M E T E R S
==============================

DENSITY FUNCTIONAL POTENTIAL (scf)
   LDA:                              VWN
```

```
   Gradient Corrections:              Becke88 Perdew86

SPIN  (restricted / unrestr.)
   Molecule:                          Restricted
   Fragments:                         Restricted

OTHER ASPECTS
   Relativistic Corrections:          scalar (ZORA,FrozenCore)
   Core Treatment:                    Frozen Orbital(s)

   Electric Field:                    ---

   Magnetic Field:                    ---


Fragment File(s)
----------------
c:
        file : t21.C
        jobid: ADF 2000.01  RunTime: Dec08-2000 00:59:25
        title: Carbon (III, 1s frozen)
o:
        file : t21.O
        jobid: ADF 2000.01  RunTime: Dec08-2000 00:59:22
        title: Oxygen (III, 1s frozen)
ti:
        file : t21.Ti
        jobid: ADF 2000.01  RunTime: Dec08-2000 00:59:13
        title: Titanium (IV, 2p frozen)
n:
        file : t21.N
        jobid: ADF 2000.01  RunTime: Dec08-2000 00:59:36
        title: Nitrogen (III, 1s frozen)
h:
        file : t21.H
        jobid: ADF 2000.01  RunTime: Dec08-2000 00:59:28
        title: Hydrogen (III)
```